University of Zurich[UZH]

Zurich Open Repository and Archive
University of Zurich
University Library
Strickhofstrasse 39
CH-8057 Zurich
www.zora.uzh.ch

Year: 2019

'Forbidden' Electrocyclizations of Diradicaloids

Šolomek, Tomáš ; Ravat, Prince ; Juricek, Michal

DOI: https://doi.org/10.1016/j.trechm.2019.08.005

Posted at the Zurich Open Repository and Archive, University of Zurich
ZORA URL: https://doi.org/10.5167/uzh-176882
Journal Article
Accepted Version

The following work is licensed under a Creative Commons: Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) License.

Originally published at:
Šolomek, Tomáš; Ravat, Prince; Juricek, Michal (2019). 'Forbidden' Electrocyclizations of Diradicaloids. Trends in Chemistry, 1(7):705-706.
DOI: https://doi.org/10.1016/j.trechm.2019.08.005

"Forbidden" Electrocyclizations of Diradicaloids

Tomáš Šolomek,[1] Prince Ravat[2] and Michal Juríček[3,*]

[1]Department of Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland
[2]Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany
[3]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

*Correspondence: michal.juricek@chem.uzh.ch (M. Juríček)

Origin

Electrocyclizations are a subclass of pericyclic reactions where, as a net result, one π bond is transformed into one σ bond, or vice versa. These reactions obey the Woodward–Hoffmann rules that dictate the reaction mode, conrotatory/disrotatory, based on the orbital symmetry. Diradicaloid compounds violate these rules as their formally symmetry-forbidden thermal electrocyclizations have unusually low activation energies and proceed at temperatures below ambient. Why?

Reaction Mechanism

The rotatory mode and stereochemical outcome of a thermal electrocyclization are governed by the symmetry of the highest occupied molecular orbital (HOMO). As a result, 4π electrocyclic reactions typically proceed in a conrotatory mode, while 6π reactions in a disrotatory mode. Diradicaloid compounds characterized by low-lying excited states are a rare exception to the Woodward–Hoffmann rules. Michl *et al.*, who investigated 4π electrocyclization of pleiadene (**1**), suggested in 1978 that the low energy of the first doubly excited state of **1** is responsible for the low activation energy (E_a = 21.3 kcal mol^{-1}) of the formally forbidden disrotatory process. Recently, 6π conrotatory electrocyclizations of biphenalenylidene (**2**; Kubo *et al.*) and cethrene (**3a** and **3b**; Juríček *et al.*) were found to have surprisingly low E_a values. The striking observation in these cases is that DFT calculations (~23–24 kcal mol^{-1}) fail to reproduce the experimental E_a values or their trend (15.7, 14.1 and 20.3 kcal mol^{-1} for **2**, **3a** and **3b**, resp.), although DFT can indirectly account for configurations other than ground state via broken spin-symmetry formalism. Considering these findings, we hypothesized that symmetry of these C_2-symmetric systems decreases along the reaction coordinate because of vibronic coupling mixing the ground and lowest singlet excited states, which might lower E_a. The presence of the C_1-symmetric transition states, which then possess partial charge-transfer character, is supported by an observed solvation effect (reactions proceed faster in more polar solvents) and the inability of single-determinantal DFT to account for this effect.

Importance

Electrocyclizations of diradicaloids have chameleonic nature and proceed in a given rotatory mode both photochemically and thermally. The mechanism of the formally forbidden thermal reactions is not fully understood and represents a challenge for experimental and theoretical chemists to test their chemical concepts and intuition. Future investigations into the nature of this unusual process can lead to development of new synthetic methods and magnetic switches.

Literature

1. Woodward, R.B. and Hoffmann, R. (1970) The conservation of orbital symmetry. Verlag Chemie: Weinheim

2. Schmidt, W. (1971) Die Valenzisomerisierung des trans-15,16-Dimethyl-dihydropyrens. Ein Beitrag zur Frage nach der Aktivierungsenergie Symmetrie-verbotener Prozesse. *Helv. Chim. Acta* 54, 862–868

3. Muszkat, K. A. and Schmidt, W. (1971) Energy profiles for ring formation- and ring opening-processes in the cis-stilbene-4a,4b-dihydrophenanthrene system. An example of the feasibility of a process forbidden by the rules of orbital symmetry conservation. *Helv. Chim. Acta* 54, 1195–1207

4. Steiner, R. P. and Michl, J. (1978) π,π-Biradicaloid hydrocarbons. The pleiadene family. 3. A facile symmetry-forbidden thermal conversion of a polycyclic butadiene moiety to a cyclobutene. *J. Am. Chem. Soc.* 100, 6413–6415

5. Uchida, K. *et al.* (2016) Biphenalenylidene: isolation and characterization of the reactive intermediate on the decomposition pathway of phenalenyl radical. *J. Am. Chem. Soc.* 138, 2399–2410

6. Ravat, P. *et al.* (2016) Cethrene: a helically chiral biradicaloid isomer of heptazethrene. *Angew. Chem. Int. Ed.* 55, 1183–1186

7. Šolomek, T. *et al.* (2018) Cethrene: the chameleon of Woodward–Hoffmann rules. *J. Org. Chem.* 83, 4769–4774

8. Ravat, P. *et al.* (2018) Dimethylcethrene: a chiroptical diradicaloid photoswitch. *J. Am. Chem. Soc.* 140, 10839–10847

Figure 1.

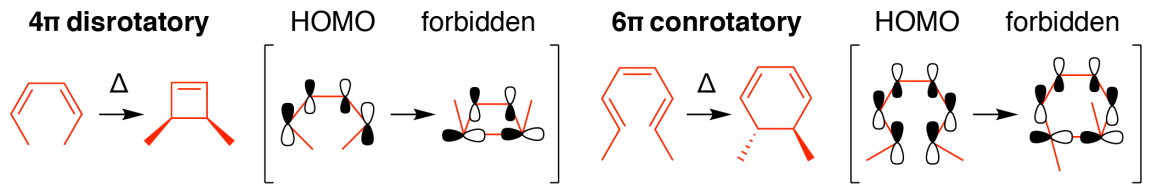

Figure 2.